Expanding Sample Environments: *The High Pressure Perspective*

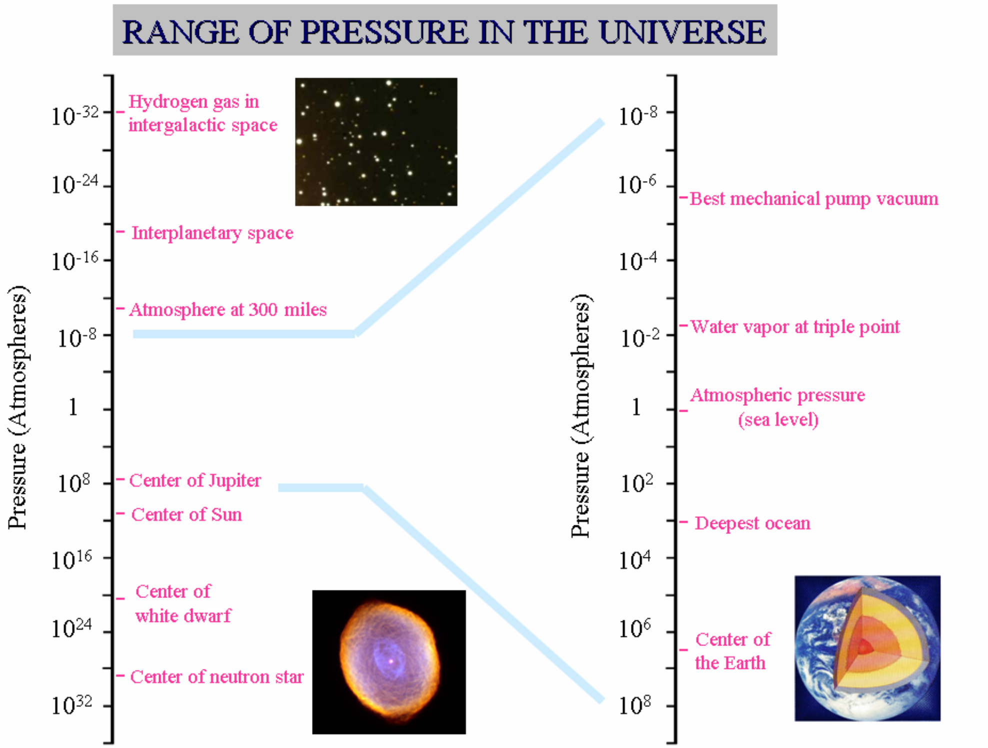
Russell J. Hemley

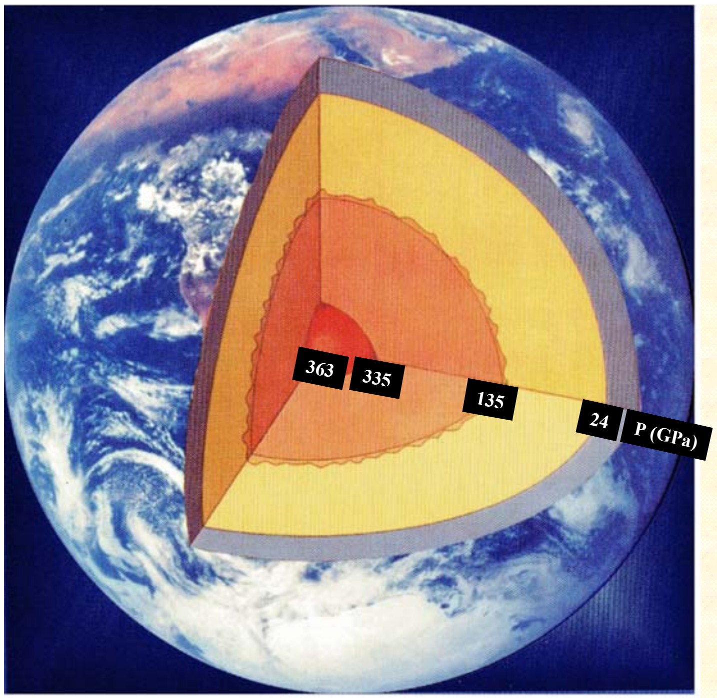
Geophysical Laboratory
Carnegie Institution
Washington, DC

OUTLINE

I. Motivation
II. Five Examples
III. An Important Technological Advance
IV. Technical Challenges

Duplicating sample environments found throughout the visible universe: the pressure variable

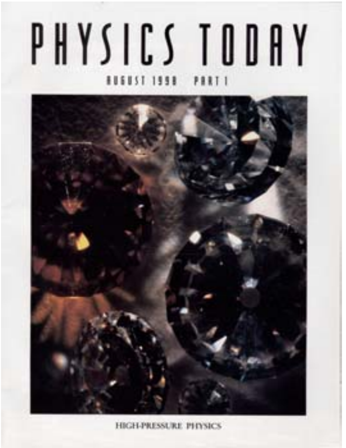


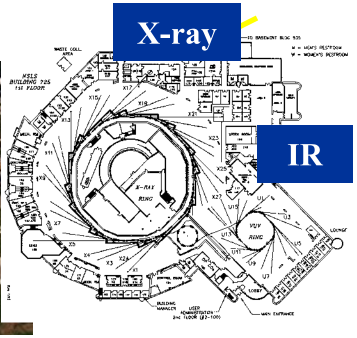


➢ *VARY INTERATOMIC, INTERMOLECULAR, AND INTERPARTICLE DISTANCES OVER A BROAD RANGE*

- ***Diverse applications***
- ***New physical and chemical phenomena***
- ***Novel materials***
- ***Nanomaterials***

Numerous techniques are being used to explore materials under extreme conditions





SYNCHROTRON METHODS

Diffraction
- SINGLE CRYSTAL, POLYCRYSTALLINE
- RADIAL, SUB-MICRON

Spectroscopy
- EMISSION, EXAFS, XANES

Inelastic Scattering
- PHONON, ELECTRON, NUCLEAR

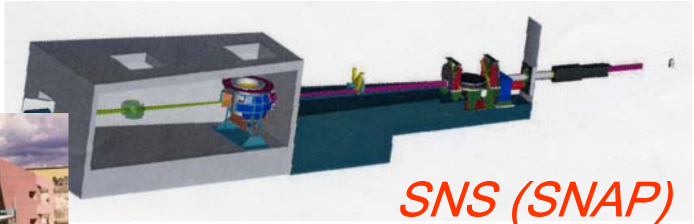
Radiography
- MICRO, MACRO

Infrared Spectroscopy
- ABSORPTION, REFLECTIVITY, EMISSION

NEUTRON METHODS

Diffraction
- SINGLE CRYSTAL, POLYCRYSTALLINE
- MAGNETIC

Inelastic Scattering
- PHONON

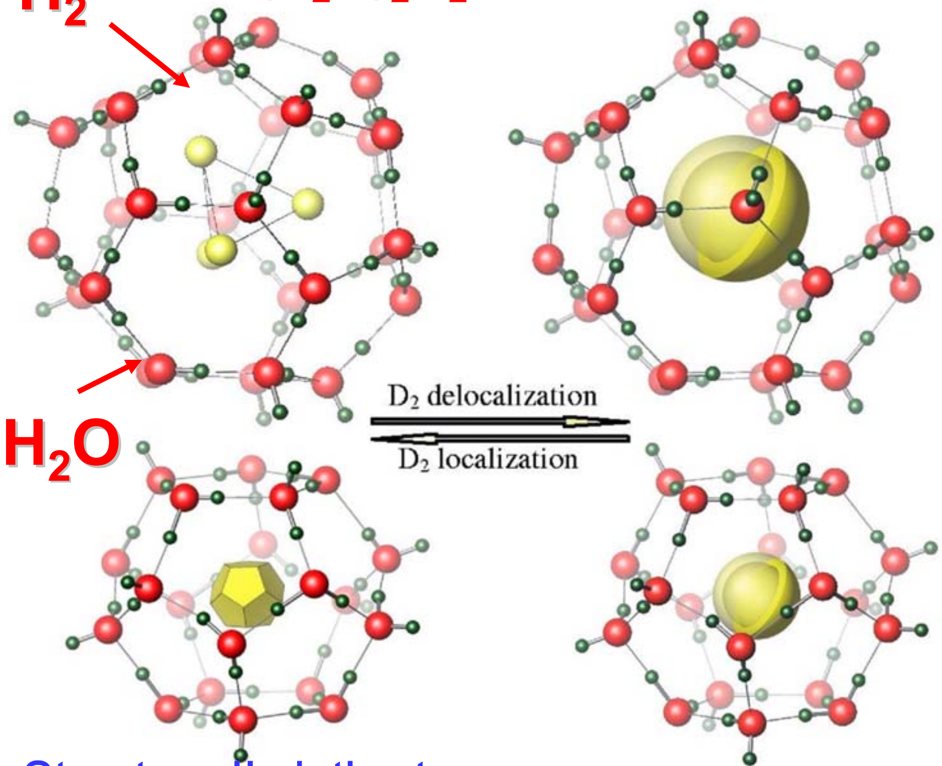


Focusing is key!

Novel hydrogen-rich clathrates and compounds have been synthesized

EXAMPLE #1

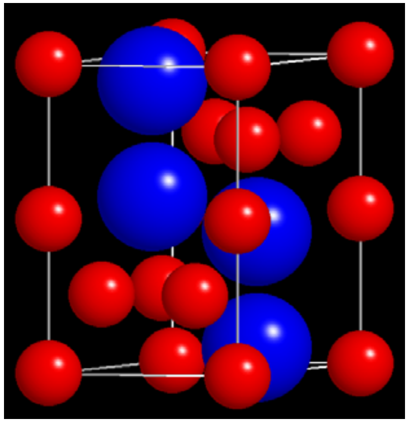
$(H_2O)_2H_2$ Clathrate



- Structure II clathrate
- Novel H_2 (D_2) clusters
- Stable at ambient pressure (<145 K)
- Match H_2 in interstellar clouds
- Hydrogen storage (5.3 wt % H_2)

[W. Mao *et al., Science* 297, 2247 (2002); Lokshin et al., *Phys. Rev. Lett*. 93, 125503 (2004)]

Methane-Hydrogen Compounds



$CH_4(H_2)_2$

[Somayazulu *et al. Science* 271, 1400 (1996)]

$(H_2)_4CH_4$ contains the largest amount of hydrogen of any known compound recovered to 0.5 GPa and <100 K [W. Mao *et al. Chem. Phys. Lett. 402, 66* (2005)]

FUTURE

- ***Chemical tuning to expand stability***
- ***Large volume production***
- ***Integration in devices***

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Pressure provides a means to study stability and transformation mechanisms

EXAMPLE #2

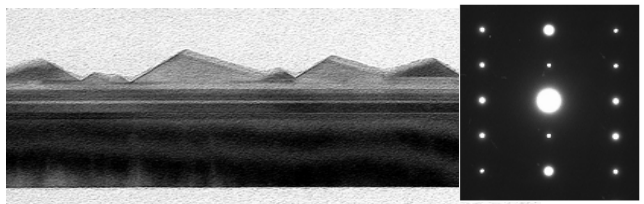
Pressure effects on ZnS nanowires:

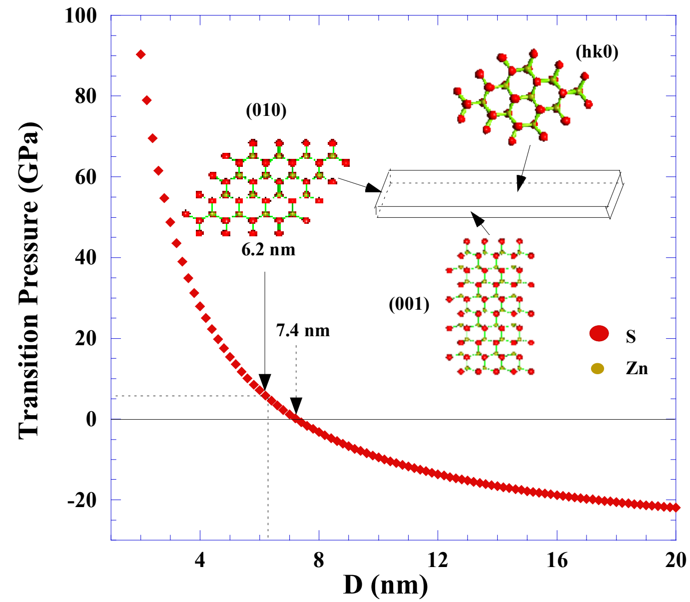
X-ray Diffraction

[Wang *et al.*, *Nature Mater.*, submitted]

Sphalerite Nanoparticle

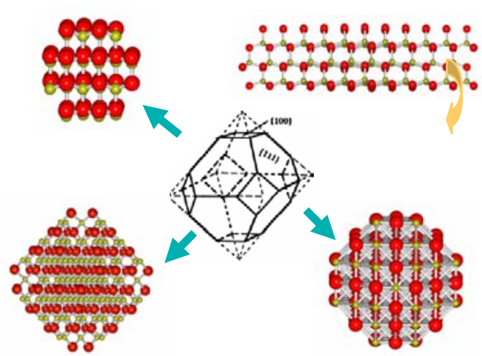
Rocksalt Nanoparticle





Hexagonal particle

Hexagonal nanobelt



(100)+(111)

(hk0) dominated

1. Low energy surface structure
2. Stabilizing both in belt shape and structure up to 6.8 GPa
3. Rapid explosive transition mechanism

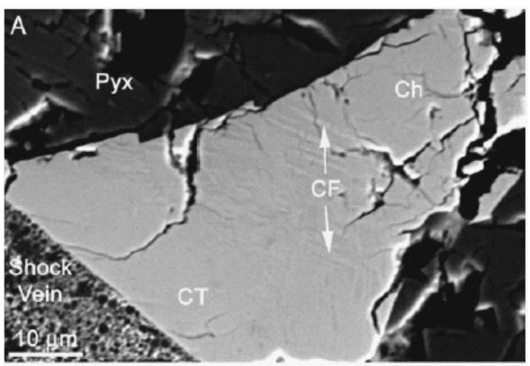
FUTURE

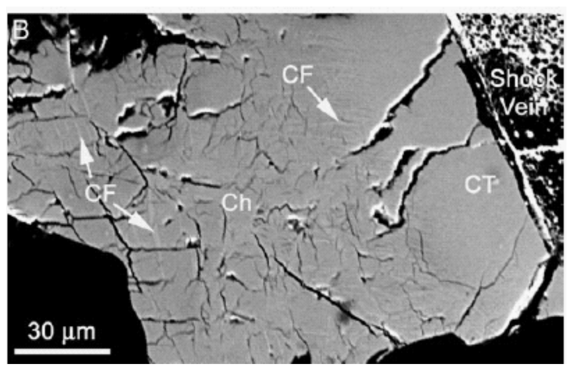
- ***Making and recovering new materials***
- ***Understanding interfaces and particle contacts***

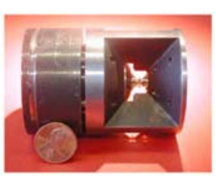
These methods are opening up the new field of micro/nano-mineralogy

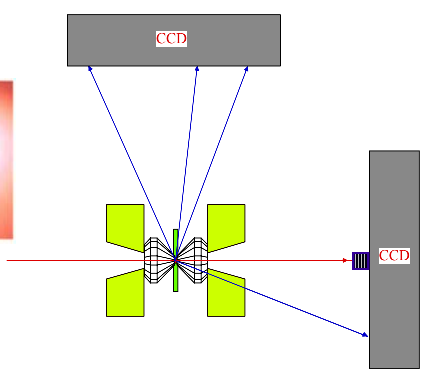
- *Observations of new materials in meteorites*
- *Micro- to nano-size inclusions*
- *Texture development*
- *Complementary high P-T diffraction*

$FeCr_2O_4$ [Ming *et al.*, *PNAS* 100, 14651 (2003)]





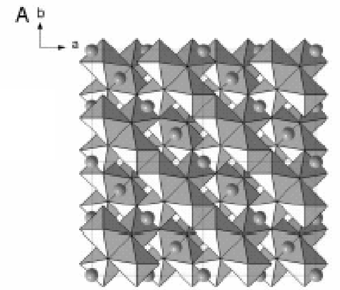




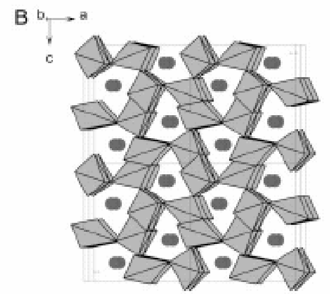
- High-pressure micro and with panoramic cells for both forward and 90 Laue diffraction and spectroscopy

[Larsen *et al.*, *Nature* 415, 887 (2002)]

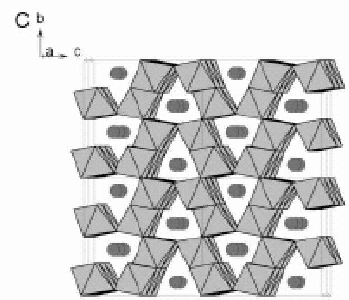
EXAMPLE #3



Spinel-type



Calcium titanite -type



Calcium ferrite -type

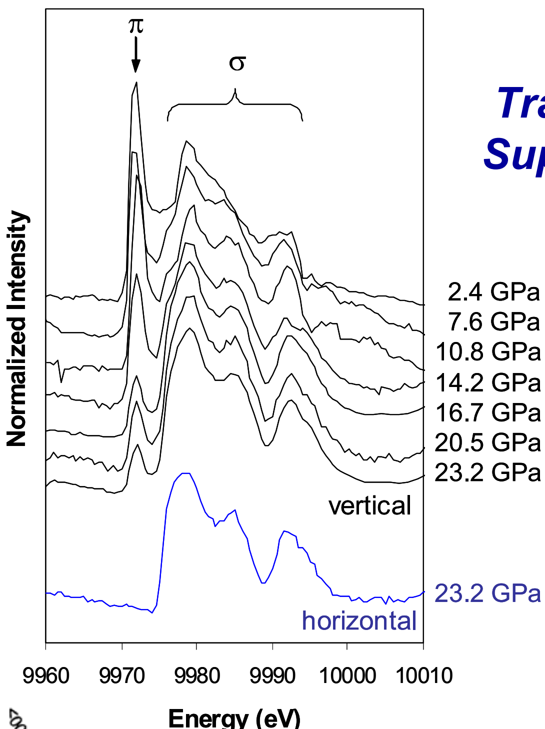
FUTURE

- *Nanometer scale x-ray tomography*
- *Extension to in situ high P-T study*

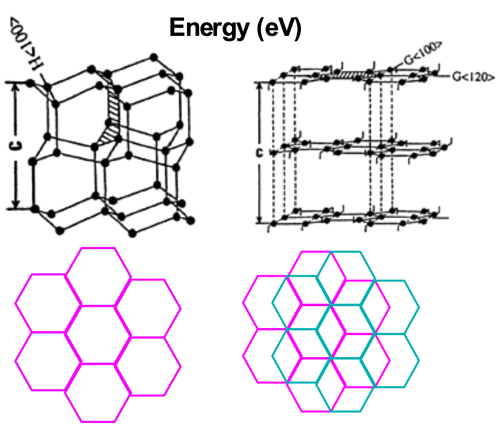
Pressure-induced changes in bonding state are revealed by x-ray spectroscopy and inelastic scattering

EXAMPLE #3

Bonding Changes by Inelastic Scattering

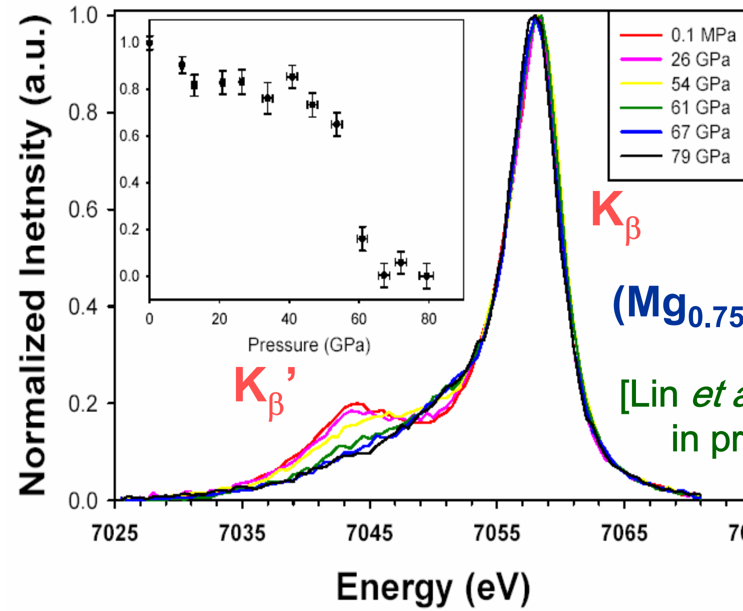


Transformation to Superhard Phase of Graphite



[Mao *et al. Science* 302, 425 (2003)]

Spin State by X-ray Emission



$(Mg_{0.75}Fe_{0.25})O$

[Lin *et al., Nature*, in press]

The loss of the satellite peak ($K\beta$') above 60 GPa indicates the collapse of magnetization.

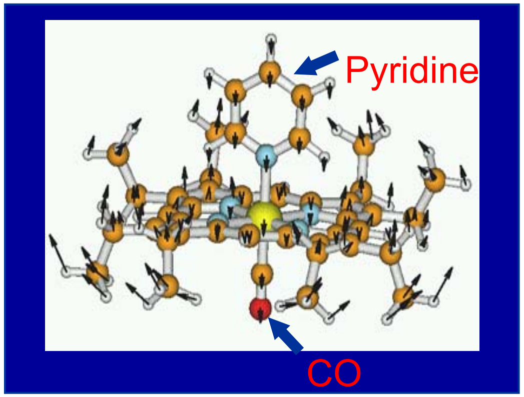
FUTURE

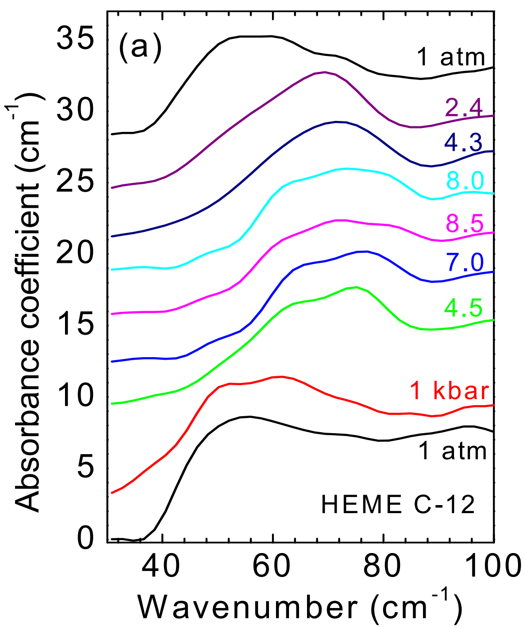
- **Applications to nanomaterials under pressure**
- **Extend spectroscopies to imaging and to higher pressure**

These techniques can probe structure-property relations in biological structures under pressure

EXAMPLE #4

Heme Doming Mode

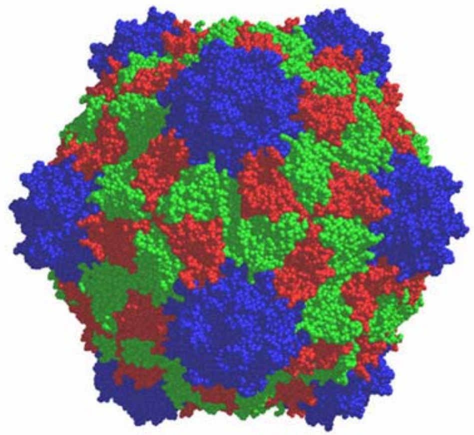


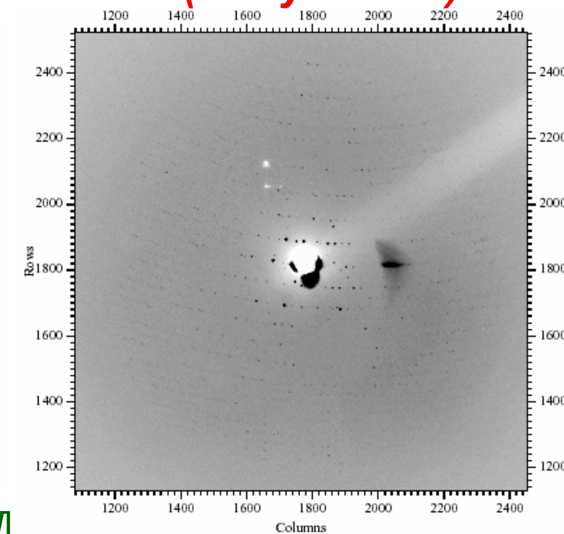


[Klug *et al.*, *PNAS*, 99, 1256 (2002)]

Doming modes and dynamics of model heme compounds: first high pressure infrared studies in THz region

Cow Pea Mosaic Virus to 5 kbar (X-ray and IR)





[Lin *et al.*, *to be published*]

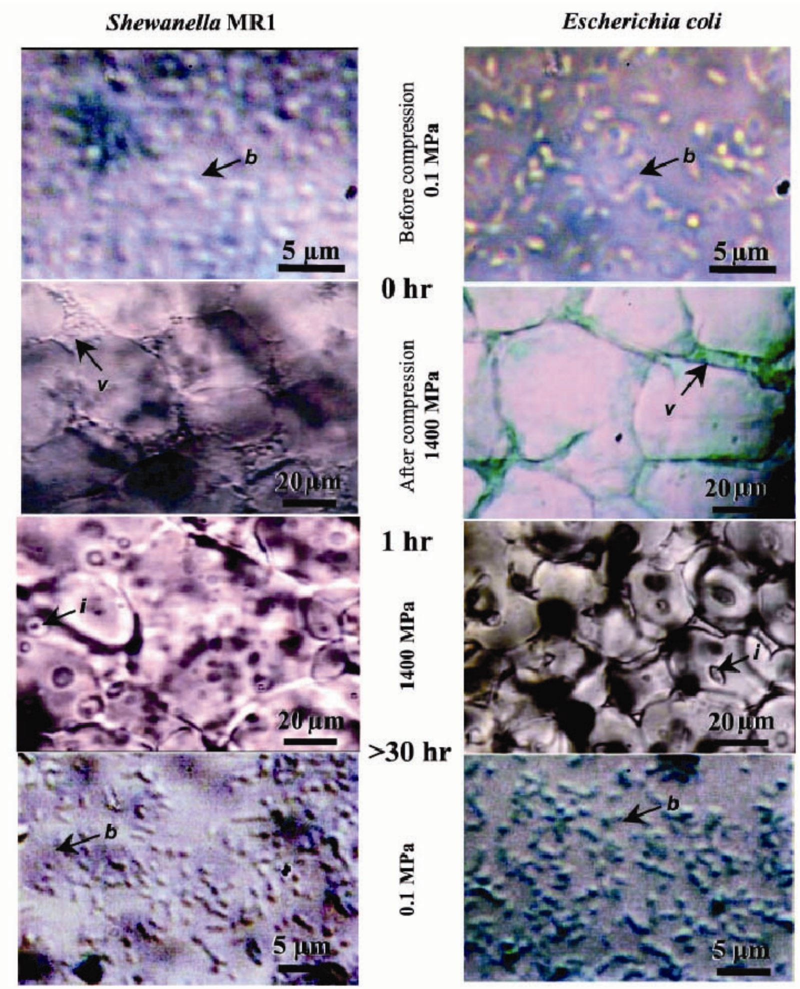
FUTURE

- **Time-resolved diffraction and spectroscopy**
- **Extension to high-pressure neutron scattering**
- **More complex structure**
- **Large sample volumes**

Microbes are viable at significantly higher pressure than previously thought

EXAMPLE #5

DIRECT OBSERVATIONS OF MICROBES TO 20 kbar



FUTURE

- IR/optical/x-ray imaging with *P-T-t*
- Tomography of single cells under stress
- "Test-tube" study of microbial evolution and adaptation
- Combined with other probes (e.g., quantum dots)
- High-pressure microbiology and genetics

[Sharma *et al*., *Science* 295, 1514 (2002)]

There have been important advances in diamond fabrication techniques

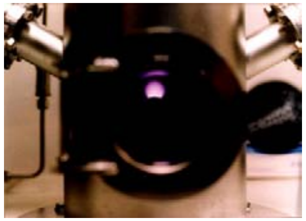
LIMITATIONS OF CURRENT TECHNOLOGY:

- **Larger sample volumes needed (neutron scattering, x-ray inelastic scattering, THz spectroscopy, NMR)**

- **Higher pressures (1 TPa or 10 Mbar) and temperatures (>1 eV)**

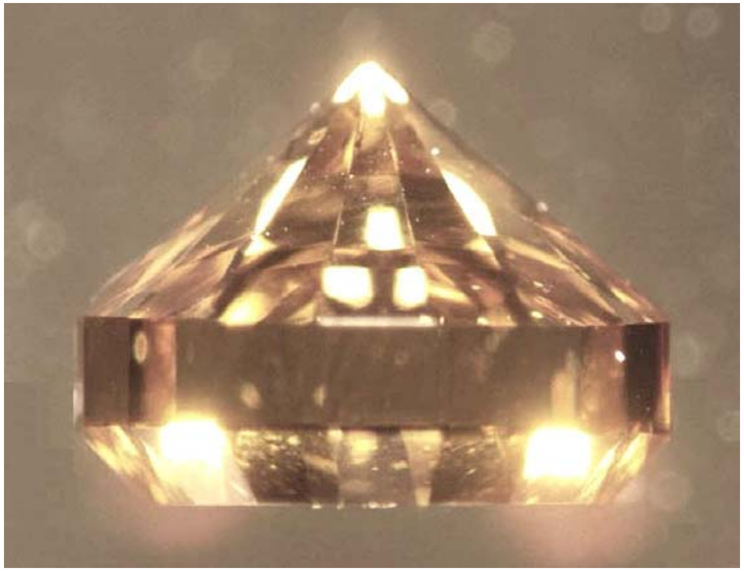
- **Further improve accuracy/precision and applications of multiple simultaneous**

Diamond Growing in a Plasma Reactor



Growth of Single Crystal Diamond by Homoepitaxial Chemical Vapor Deposition

[Yan *et al*. *PNAS* 99, 12523 (2002)]



- 2.45 mm high
- 0.28 carats
- 0.45 mm seed
- <u>Grown in 1 day</u>

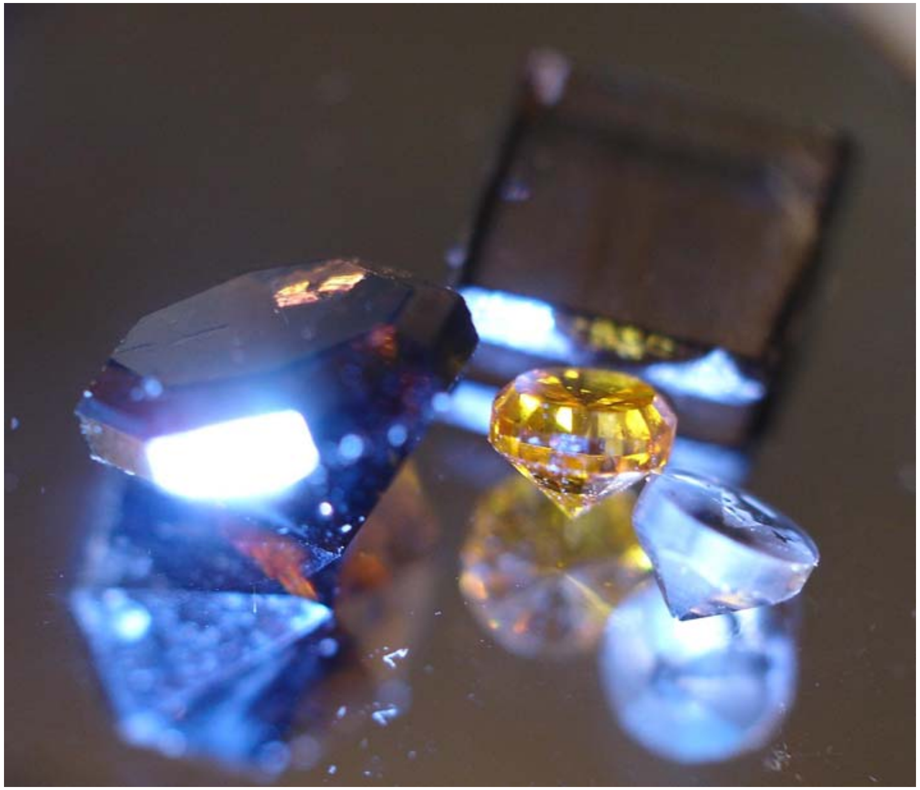
CVD single crystals are ultratough and/or ultrahard

[Yan *et al*. *Phys. Stat. Sol.* 201, R27(2004)]

Single-crystal CVD anvils generate multimegabar (>100 GPa) pressures

[W. Mao *et al*., *Appl. Phys. Lett.* 83, 5190 (2003)]

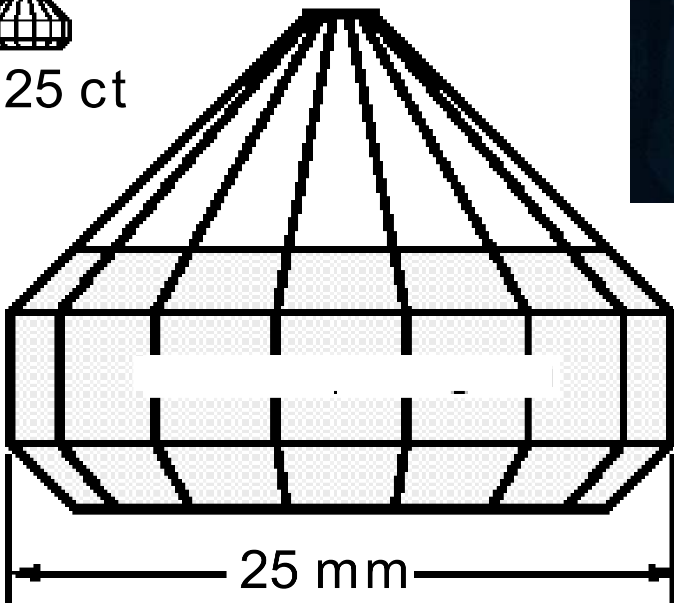
Half-inch (10 carat) diamond single crystals have been fabricated



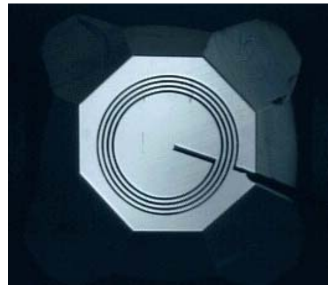
Prepare arbitrary shapes:
anvils, blocks, plates

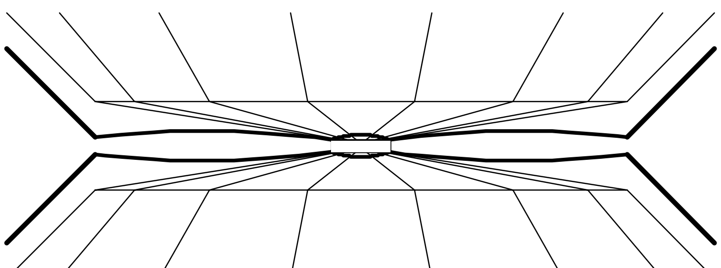
Half-inch (10 carat) diamond single crystals have been fabricated

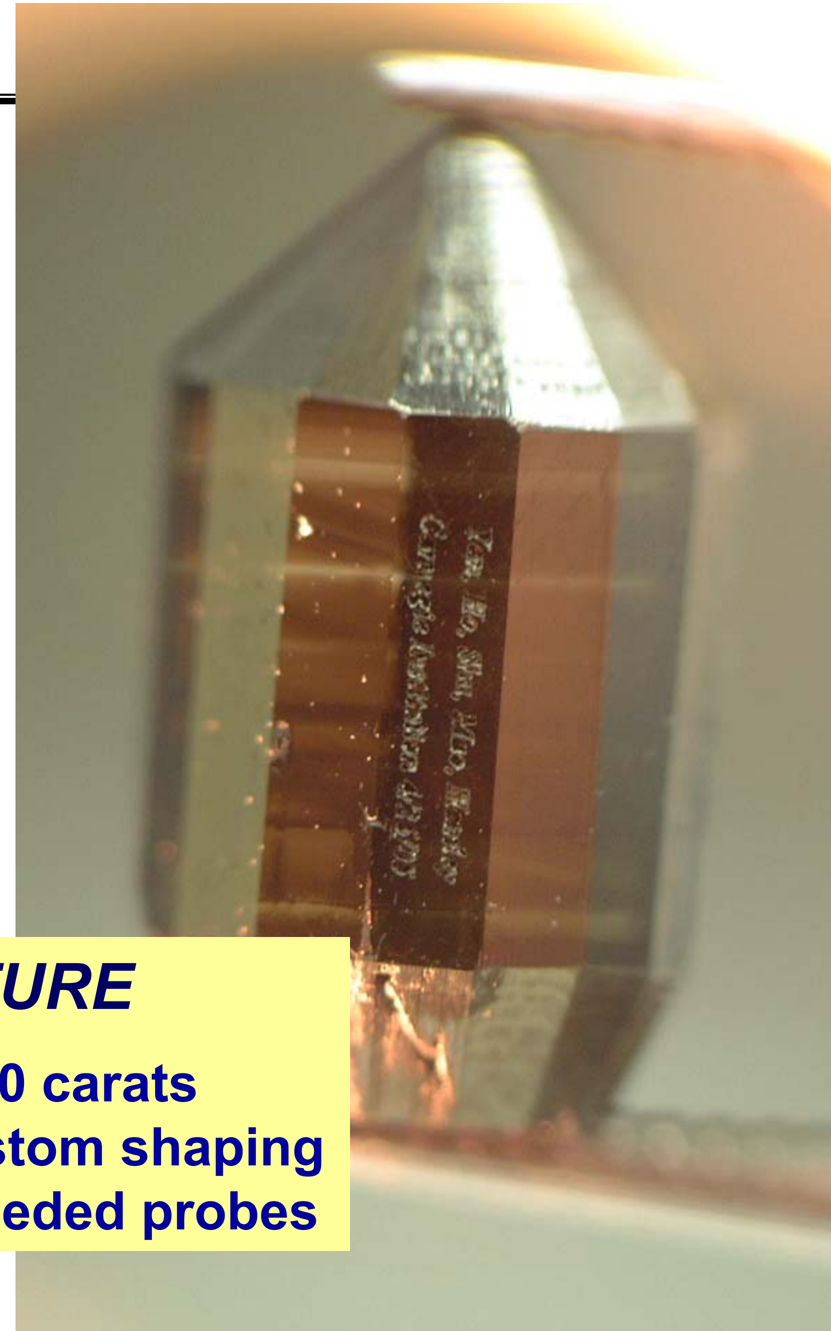
0.25 ct



100 ct







FUTURE

- **>100 carats**
- **Custom shaping**
- **Imbeded probes**

Summary: *Technical Challenges*

1. **New scale of sample environments:**
   large volume (>1 mm^3 samples) at 300 GPa,
   1 mK to 1 eV temperatures.
   → ***A new generation of devices based on >100 carat diamonds***
2. **Moving from single-phase diffraction/scattering to imaging of materials under extreme conditions**
   → ***Submicron beams with new generation of devices***
3. **Chemical dynamics under extreme conditions**
   → ***Exploiting time domain (coherent sources)***
   → ***Combined static/dynamic compression***
4. **Integration with other techniques**
   → ***Magnetic fields, intense lasers, etc.***